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CORRELATION-BASED APPROACHES TO TIME-RESOLVED FLUORIMETRY.(U)
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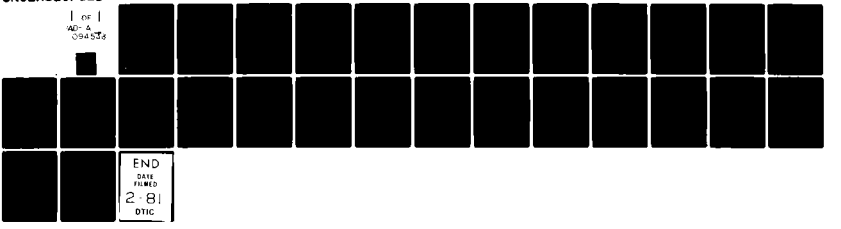

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In the past two years, several new techniques have been introduced for the measurement of nanosecond and subnanosecond fluorescence processes (1-5). Because these methods use relatively simple instrumentation and offer exceptional time resolution and accuracy, they compete favorably with more established approaches. In this paper, an introduction to these new methods is provided and their capabilities and limitations assessed.

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# CORRELATION-BASED APPROACHES TO TIME-RESOLVED FLUORIMETRY

by

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Prepared for Publication

in

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In the past two years, several new techniques have been introduced for the measurement of nanosecond and subnanosecond fluorescence processes (1-5). Because these methods use relatively simple instrumentation and offer exceptional time resolution and accuracy, they compete favorably with more established approaches. In this paper, an introduction to these new methods is provided and their capabilities and limitations assessed. Because the new correlation-based techniques have their bases in a field termed linear response theory, let us briefly review the basic precepts of that field.

## LINEAR RESPONSE MEASUREMENTS

During the measurement of fluorescence decay curves, one attempts to determine the response of a fluorescing molecule to a pulse of radiation which perturbs it. That is, the perturbing light pulse creates a transient over-population of a chosen excited state, which then decays with time. In turn, this decay can be monitored by following the time-dependent fluorescence of the molecule. This time-dependent decay, which is the information sought, can be viewed as the impulse response function of the fluorescing sample, according to linear response theory (6). Conveniently, individuals working with linear response theory have developed alternative approaches to obtain the same kind of information; these alternative schemes can be applied profitably to time-resolved fluorimetry.

To understand these alternative schemes, let us view impulse-response measurements from a more general viewpoint. As seen in Figure 1, an impulse response is elicited from any system which is perturbed by an extremely brief (impulsive) energy source. Ideally, the impulsive perturbation should be

infinitely narrow, that is, should approach a mathematical delta function. If this goal is realized, the Fourier transform of the perturbing pulse will be flat; in other words, it will contain all frequencies. Therefore, the response elicited by the perturbation should also contain all frequencies, except those which have been distorted, attenuated, or phase shifted. Accordingly, it seems reasonable that alternative perturbing waveforms could be used to obtain the same information, obviating the need for brief, high-energy pulses. Of course, the alternative waveform, like the impulse, must contain a broad range of frequencies. The most general such waveform is broad-band or "white" noise.

White noise, like a delta function, contains all frequencies. However, the frequency components in the noisy waveform are unrelated in phase. Therefore, the response of the tested system to a noisy perturbation will also appear noisy. However, the noisy response will <u>not</u> be the same as the perturbing waveform, but will have frequency components which are attenuated, distorted, and phase shifted much like those in the impulse when it is employed. From these considerations, it is evident that the noisy response contains the same information as the impulse response function but that the information has a different form. The "trick" is then to process the information in the noisy response to make it appear like the more familiar impulse response.

The trick to be used in this case is correlation (7). As portrayed in Figure 2, autocorrelation of a random waveform (white noise) produces a delta function. This result derives from the fact that autocorrelation phase relates all frequency components in a waveform. When this phase registration occurs, all the frequency components add constructively at the phase-related

point. However, at all other locations, the waves cancel each other, to produce a net value of zero. Therefore, the overall result is the production of a sharp, impulse-like waveform.

Similarly, it is possible to produce the impulse response function simply by cross-correlating a random waveform which perturbs a tested system with the apparently noisy response it elicits. This behavior, shown schematically in Figure 3, can be understood by recalling that autocorrelation is merely the cross-correlation of a waveform with itself. In the present case, however, the random perturbing function is being cross-correlated with a waveform that resembles it, but which has removed from it or changed within it several frequency components. Therefore, the resulting correlation waveform cannot rise and fall with infinite sharpness as does the delta function, but instead changes more slowly. In other words, it is identical to the impulse response function.

## LINEAR RESPONSE FLUORIMETRY

Translating these concepts to the measurement of fluorescence lifetimes establishes instrumental requirements for a correlation fluorimeter (2). Such a fluorimeter might appear as in Figure 4. In the correlation fluorimeter, a randomly modulated light source is employed instead of one which is pulsed. In turn, the random fluctuations in light intensity from the source are cross-correlated with the apparently random fluctuations in fluorescence which it generates; from the correlation computer an output should result which is the desired fluorescence decay curve. As will be shown later, some configurations will permit the use of a spectrum analyzer in place

of the correlation computer. Because the correlation computer will probably be electronic in nature, it must process electrical rather than optical signals and will therefore require a fast photodetector to monitor fluorescence fluctuations; fluctuations in the modulated source intensity will be monitored from the source modulator itself. In the instrument, excitation and emission monochromators would probably be incorporated to enable the experimenter to select specific wavelengths to excite the desired fluorophore and at which fluorescence is to be measured.

Because fluorescence decay curves are seldom longer than several nanoseconds, stringent instrumental requirements are placed on the correlation fluorimeter of Figure 4. First, the monitored fluorescence fluctuations must be observed on a nanosecond time scale, requiring an extremely fast correlation computer. In addition, because of the necessary short-term nature of the fluctuations, the source must be modulated at frequencies beyond 1 GHz. Let us first examine sources which exhibit such high-frequency fluctuations and might therefore prove suitable for correlation fluorimetry.

## Sources

The most general source for producing high-frequency fluctuations is a simple white-light lamp like a tungsten bulb. Although such a lamp cannot be modulated at high frequencies, it inherently produces quantum noise which is by nature extremely broadband (i.e. white). Unfortunately, the light from such a source also generates shot noise from any photodetector used to monitor fluorescence fluctuations. Careful mathematical analysis (8)

then shows that such a source, if used with correlation fluorimetry, would yeild under optimal conditions a signal-to-noise ratio no higher than 1! Clearly, the source would be unsuitable for such an application.

What is needed is a source whose modulation amplitude is much higher than would be produced by quantum noise. Such a source is a C.W. laser. Laser mode noise, which is often discussed but poorly characterized, can be qualitatively described as the "beating" of laser modes with each other. This beating produces in the output of the laser an apparent amplitude modulation at discrete frequencies separated by an amount equal to the laser's mode spacing. Moreover, these beats extend to frequencies as high as the laser's emission bandwidth. Because the mode spacing in a laser is equal to $\frac{c}{2L}$, where c is the speed of light and L is the distance between the laser's mirrors, a C.W. laser will appear to be amplitude modulated at frequencies of $\frac{c}{2L}$, $\frac{2c}{2L}$, $\frac{3c}{2L}$, ... $\frac{nc}{2L}$, where n is the number of modes oscillating within the laser. For typical ion lasers (e.g. an argon ion laser), L is $\sim$ 1 meter, making c/2L = 150 MHz. Moreover, in such a laser, as many as 30 modes oscillate, indicating that the laser will appear to be amplitude modulated at discrete frequencies of 150 MHz, 300 MHz, 450 MHz, etc., up to frequencies as high as 4.5 GHz. Because these amplitude modulations are relatively large, the laser serves as a nearly ideal source for correlation fluorimetry.

Cross-correlation computer

Calculation of the correlation function for correlation fluorimetry has taken two forms. In the first approach, it is recognized that nano-

second correlators are relatively complex and an alternative function is calculated from which the correlation waveform can be deduced. In the second approach, the correlation function is itself evaluated directly.

Spectrum Analysis Approach. The first of these approaches is based upon the fact that the autocorrelation function of a waveform is the Fourier transform of its power spectrum. Whereas it would seem at first glance difficult to determine a nanosecond correlation function, it is relatively straightforward to measure a gigahertz power spectrum, simply through use of a microwave spectrum analyzer. If desired, a waveform related to the impulse response function (fluorescence decay curve) can then be calculated by Fourier transformation of the measured power spectrum.

An instrument useful for correlation fluorimetry based on a power spectrum measurement is portrayed in Figure 5 (1). To appreciate how this instrument performs, let us perform two hypothetical experiments. In the first experiment, the sample cell shown in Figure 5 will be filled with a scattering suspension, so that the photodetector monitors fluctuations in scattered radiation which mimic those in the laser. In this case, the microwave spectrum analyzer will produce a plot which shows the frequency composition of the laser's fluctuations; such a plot reveals that the laser's output radiant power fluctuates over a broad range of discrete frequencies.

In the second experiment performed with the apparatus of Figure 5, we will monitor the fluctuations in sample fluorescence induced by the fluctuating laser light. Although the laser's discrete-frequency fluctuations all occur simultaneously, we can understand their effect by considering the frequency components individually. For the lowest frequency components (recall $\frac{c}{2L}$ = 150 MHz for a laser whose cavity is 1 meter long), the fluorescing

molecule's excited state would be short enough in lifetime to enable it to follow the variations in laser output intensity. Therefore, the excited-state population of the fluorophore will increase and decrease as the laser varies, producing a similar fluctuation in fluorescence. Accordingly, the spectrum analyzer will register a large amplitude in fluorescence fluctuation at that particular frequency. In contrast, high-frequency fluctuations in the laser cannot be followed by the fluorophore's excited-state population, because of the finite excited-state lifetime. Accordingly, there will be no fluctuations in fluorescence at the high frequencies and the amplitudes at those frequencies plotted by the spectrum analyzer will be low. Clearly, between these extremes a slow roll-off will occur. More importantly, the form of the roll-off can be understood by recognizing that it is the frequency-domain equivalent of the time-domain exponential decay. Thus, the roll-off should be Lorentzian, which is the Fourier transform of an exponential. Significantly, excited-state lifetimes can be found directly from the Lorentzian plot without resorting to Fourier transformation into the time domain. Using suitable units for the horizontal axis, is is possible to extract the excited-state lifetime as simply the reciprocal of the Lorentzian half-width.

The frequency-domain plots which are obtained using the power-spectrum approach are seldom as clean as those portrayed in Figure 5 (1). Instead, one finds that the discrete-frequency peaks caused by laser mode noise are not all the same amplitude, requiring that the corresponding fluorescence plots be normalized. That is, the mode-noise amplitudes at any two frequencies are often different, producing different amplitudes in the fluorescence fluctuations at those frequencies. However, at any frequency, the

fluorescence fluctuations are proportional to those in the mode noise; normalization then involves simply dividing the peak amplitudes measured in the fluorescence plot by those observed in the scattering experiment. Such normalization, it has been found (1), yields excellent Lorentzian plots from which the desired lifetime information can be extracted. Importantly, such division in the frequency domain is equivalent to deconvolution in the time domain. Deconvolution is ordinarily necessary in time-resolved fluorimetry but, significantly, becomes trivial when this method is employed.

Correlation Fluorimeter. In the second approach to correlation fluorimetry, an opto-electronic network is constructed to measure directly the cross-correlation function between the fluctuating laser source and the resulting fluorescence variations. A simplified schematic diagram for such a device is shown in Figure 6. To understand the operation of this correlation fluorimeter, it is useful to remember the nature of the correlation process, which can be represented by equation 1.

$$C_{1,2}(\tau) = \lim_{T \to \infty} \frac{1}{2T} \int_{-T}^{+T} B_1(t)\, B_2(t - \tau)\, dt \qquad (1)$$

Mathematically, correlation is simply a process involving multiplication, time shifting, and time averaging. To generate the cross-correlation $[C_{1,2}(\tau)]$ between two waveforms $[B_1(t)$ and $B_2(t)]$, the two waveforms must be multiplied, their product time-averaged, and the time average expressed as a function of a delay or displacement ($\tau$) between the two waveforms. This mathematical operation is implemented in a straightforward way in the instrument of Figure 6. Fast photodetectors are employed to monitor the

laser and fluorescence signals, respectively, and these signals are sent to an opto-electronic network which performs the cross-correlation. Multiplication, which must be done in an extremely high-speed system, is accomplished in a microwave mixer, a common component which serves well as a multiplier over several decades. After this multiplication step, time averaging is accomplished through use of a simple low-pass electronic filter. Finally, displacement of the waveforms with respect to each other can be accomplished by means of an optical delay line. That is, an increment in delay can be effected just by displacing spatially one of the detectors with respect to the other. In particular, because light travels at $3 \times 10^{10}$ cm/s, moving one of the detectors back a distance of 1 meter will delay the optical signal it receives by approximately 3 ns. Accordingly, changing the position of the detector then enables one to smoothly vary the temporal displacement between the two waveforms. A strip-chart recorder connected to the output of the averager (low-pass filter) will then trace out the fluorescence decay curve as displacement is swept (3).

To understand more readily the operation of this cross-correlation fluorimeter, let us consider using a deterministic (repetitively pulsed) input waveform rather than a random one (4). That is, let us use a mode-locked laser rather than one which operates in a C.W. fashion. In such a mode-locked (repetitively pulsed) laser, it can be shown that the time behavior of the laser's output amplitude has the same frequency composition as the mode noise in the C.W. laser, even though the waveforms are different. In particular, the output of a mode-locked laser is a train of extremely narrow pulses which appear at a rather high frequency. Typical values are

1-200 ps for the pulse width and 80-100 MHz for the pulse repetition rate. If such a laser is employed in the correlation fluorimeter, the photodetector used to monitor it will generate an electrical pulse which mimics that of the laser. In addition, the photomultiplier employed to monitor fluorescence will also produce a pulsed output in response to the laser's excitation. These waveforms are shown schematically in Figure 7. When the waveforms produced by the two photodetectors are multiplied, the product is a waveform which is zero except during the time when the laser pulse strikes the photodetector monitoring it. During that time, the output of the multiplier is proportional to the product of the amplitudes of the laser and the fluorescence decay curve. Therefore, this product signal is a time-sampled representation of the fluorescence signal at one particular time in its history. Because the laser is repetitively pulsed, this time sampling occurs over and over again, so that time averaging of the product produces a value which can be displayed on a suitable device (e.g. strip chart recorder) and which is proportional to the product of laser and fluorescence signal amplitude. Spatially displacing the detector which monitors either pulse then shifts the two waveforms temporally with respect to each other, and thereby permits sampling at a different point on the decay curve. Clearly, the D.C. (averaged) value registered on the monitoring device will also reflect this changed value. Smoothly sweeping the displacement of the two detectors should then permit the entire decay curve to be traced. In essence, the opto-electronic cross-correlator behaves like a boxcar integrator in this application (9).

Although this straightforward explanation might seem less elegant than the experiment in which a C.W. laser is employed, it can be shown that a

pulsed laser produces higher signal-to-noise ratios. Careful analysis of various modulation and detection schemes has been carried out and has shown this latter approach to be among the most useful (8).

## COMPARISON WITH OTHER TECHNIQUES

It is appropriate to compare the correlation fluorimetric approach with others commonly used for measuring excited-state lifetimes. The most common of these methods, the time-correlated single-photon technique (10), offers high time resolution, exceptionally high sensitivity, and relatively accurate lifetime measurements. Also, like the correlation fluorimetric method, it produces complete fluorescence decay curves (or their frequency-domain counterparts), enabling one to verify exponential behavior in a monitored signal. Therefore, it is with this method that primary comparison will be made.

In terms of sensitivity, one would anticipate the single-photon method to be superior. Moreover, because that method relies upon the detection of single photons, light source intensities must be very low, resulting in very little photodecomposition of a monitored sample. However, the necessary time for development of complete fluorescence decay curve is often inconveniently long with the single-photon approach, especially for long-lived fluorophores. For example, it is not uncommon for complete curves to require instrumental times as long as one hour for such a method, compared to measurement times of six seconds to one minute for correlation fluorimetry.

Time resolution in the two techniques should be comparable, especially if laser sources are employed. With such a source, the single-photon approach

would generate somewhat better temporal response (11), since it relies for time resolution upon detection only of the leading edge of a photodetector pulse; in contrast, correlation fluorimetry requires detection of the entire photodetector response curve. However, it is more common to employ high-pressure flash lamps as sources in single photon fluorimetry, leading to poorer time resolution but lower cost than found in the correlation fluorimetric method.

Perhaps the most significant advantage of the new linear-response-based techniques is their ability to measure decay times of self-luminous samples. Although such samples do not ordinarily arise in conventional solution fluorimetry (except for some phosphorescent or chemiluminescent samples), they are unavoidable when the fluorescence of atoms is measured. Understandably, the single-photon technique cannot tolerate the presence of stray photons, such as those emitted by hot atoms in a flame or by the flame itself, since such photons will cause pretriggering of the detection system and thus yield erroneous decay curves. In contrast, there is no penalty to be paid in correlation fluorimetry when luminous samples are employed, except for a slight loss in signal-to-noise ratio caused by photodetector shot noise. It is in this latter class of measurements that correlation fluorimetry should find its greatest application.

In our laboratories, we are employing such techniques for the measurement of steady-state lifetimes of atoms in vapor cells and in analytical sources such as flames and plasmas. In addition, we have found the basic concepts embodied in linear response theory to have important application in the measurement of a broad range of time-dependent chemical phenomena; these applications are currently being explored. Included among them are

new approaches to the measurement of photolytic reaction rates, radical-initiated chemical reactions, and the study of state-to-state kinetics. It is our hope and belief that these same concepts will be useful to many readers and will prove to be powerful tools in chemical analysis, measurement, and cnaracterization.

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## Figure Captions

Figure 1. Generation of an impulse response function by application of an impulse (mathematical delta function). The system under test might be an instrument, a chemical system or, in the present discussion, a fluorescing sample. In this case, the perturbing impulse is a brief pulse of exciting light.

Figure 2. Autocorrelation of a random waveform such as white noise produces an impulse.

Figure 3. From linear response theory, a system to be tested can be perturbed with a random waveform and still yield the impulse response function (fluorescence decay curve in the present study). However, it is necessary to employ cross correlation to phase relate the frequency components in the perturbing and response waveforms.

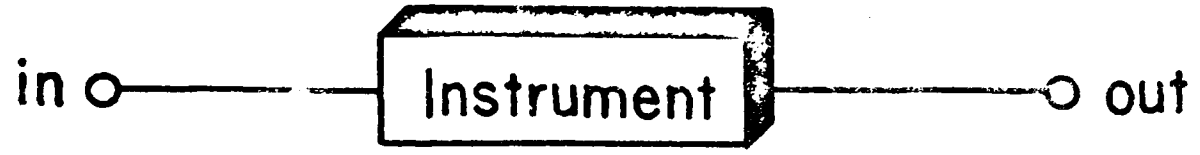
Figure 4. Schematic diagram of a hypothetical correlation fluorimeter. See text for discussion. (Reproduced with permission from reference 2)

Figure 5. Illustration of the spectrum analysis route to correlation fluorimetry. Hypothetical instrument shown on left. Top spectrum on right reflects frequency composition of laser mode noise; bottom spectrum indicates the high-frequency

roll-off in these fluctuations which would be expected in sample fluorescence excited by the laser.

Figure 6. Cross-correlation route to linear response fluorimetry. Laser might be either C.W. (containing mode noise) or mode-locked (repetitively pulsed). BS-beam splitter which reflects part of laser power to high-speed photodetector D2; C-sample cell (for molecular fluorimetry) or flame (for atomic fluorescence); D1 - fast photodetector to monitor sample fluorescence; M - microwave mixer serving as high-speed multiplier; AVG - low-pass filter serving as time averager; $\Delta X$ - spatial displacement of detector D2 which produces the time delay ($\tau$) needed in cross-correlation; $C_{1,2}(\tau)$ - cross-correlation output (fluorescence decay curve) suitable for tracing on a strip-chart recorder.

Figure 7. Schematic illustration of concept behind correlation fluorimetry. It is assumed that a repetitively pulsed laser is used as excitation source. See text for discussion.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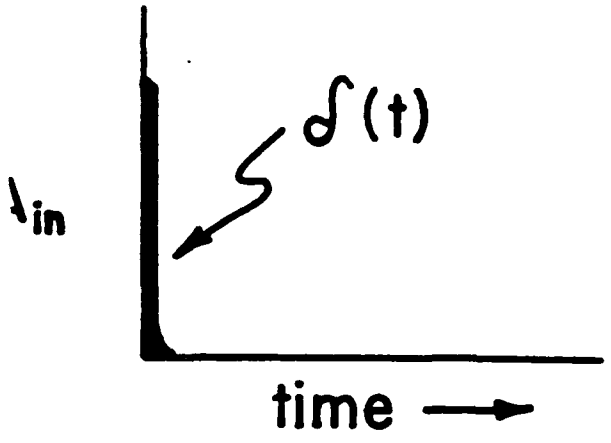
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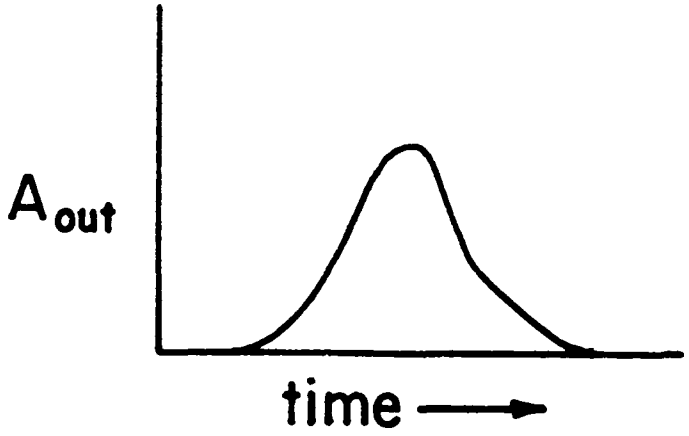
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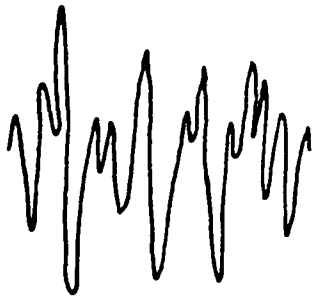

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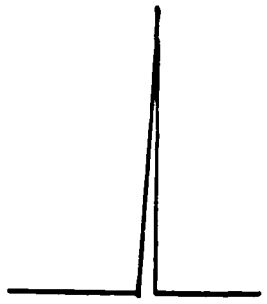

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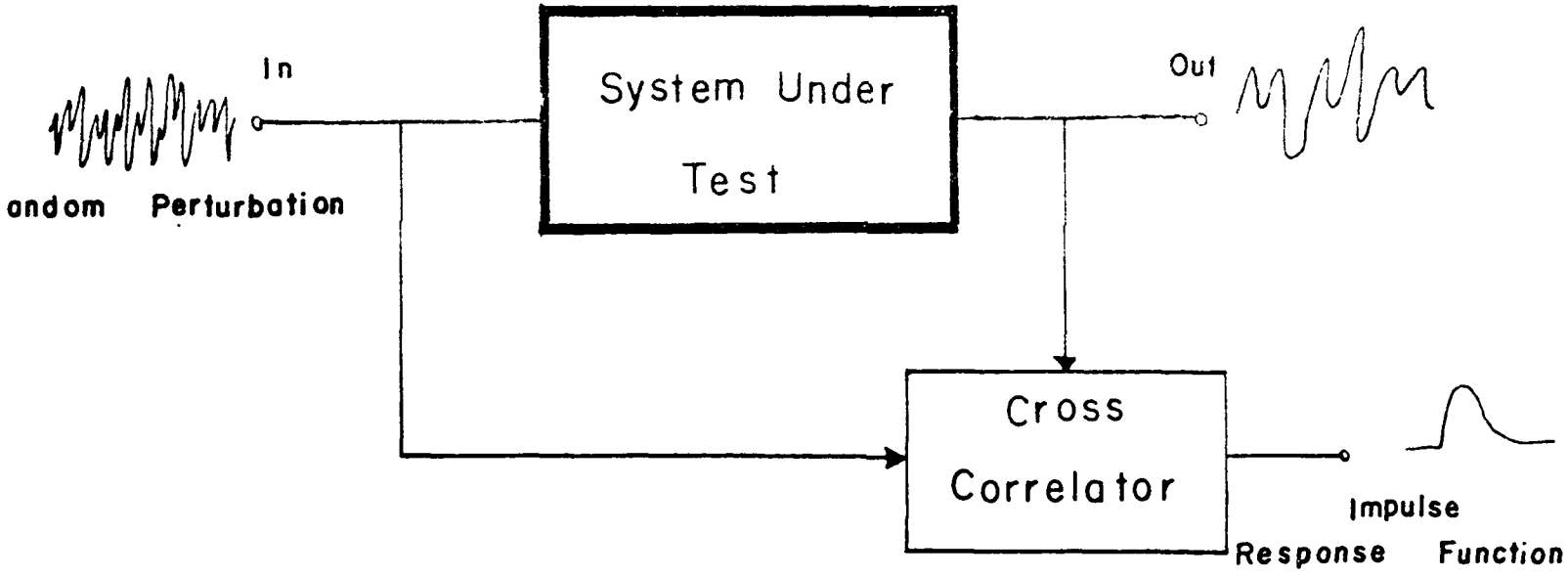
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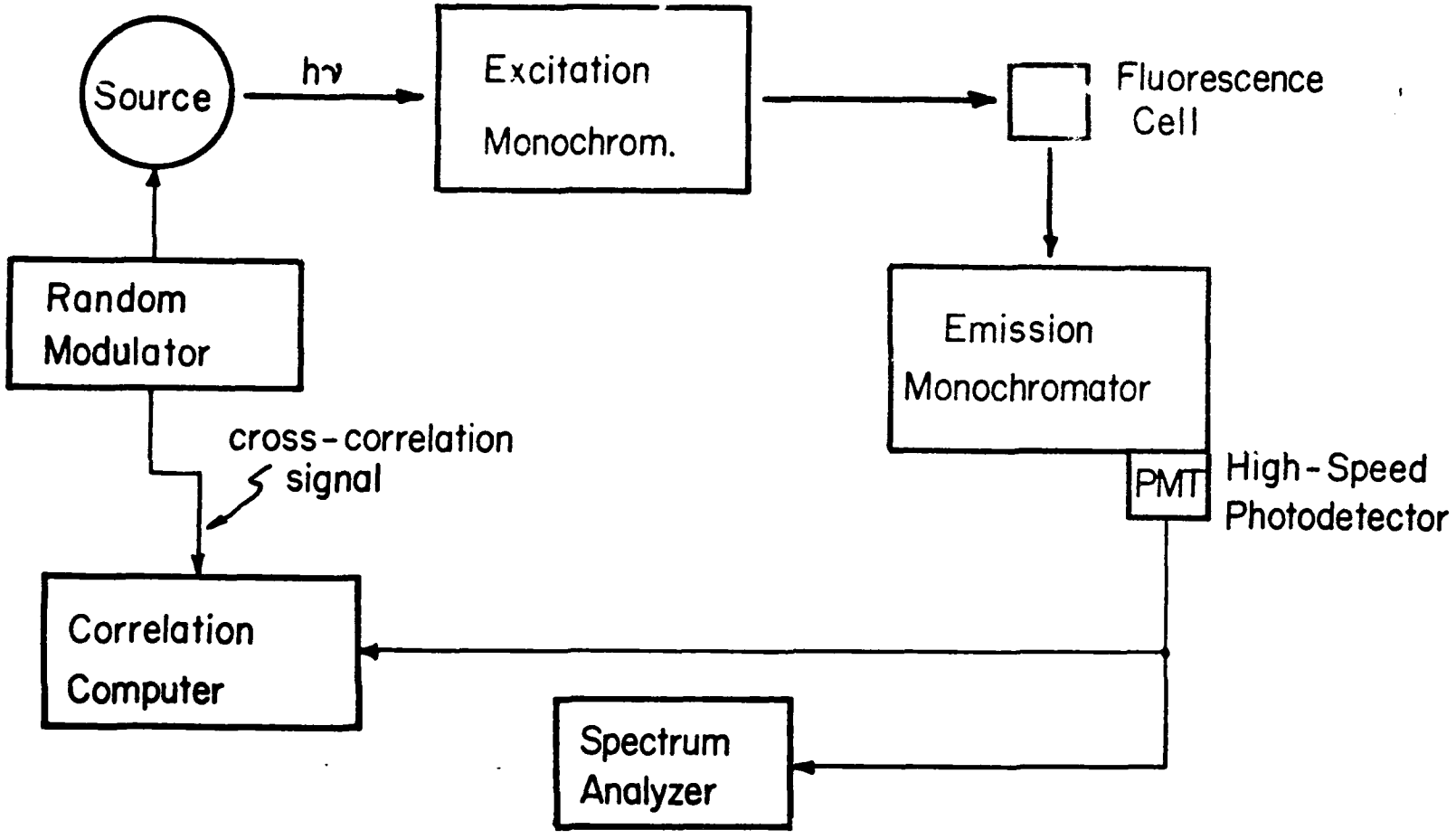
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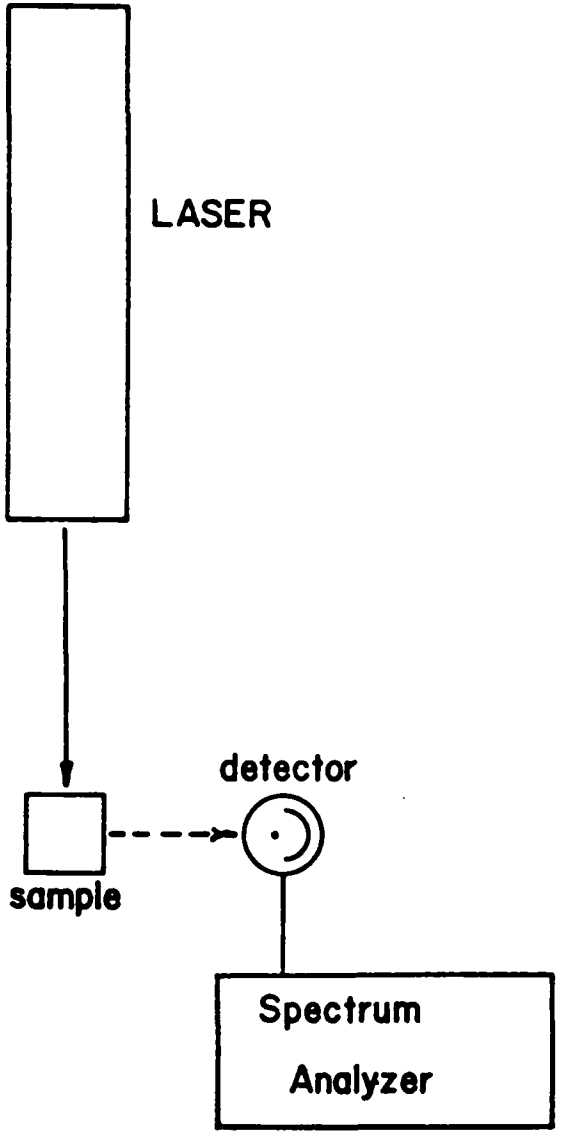
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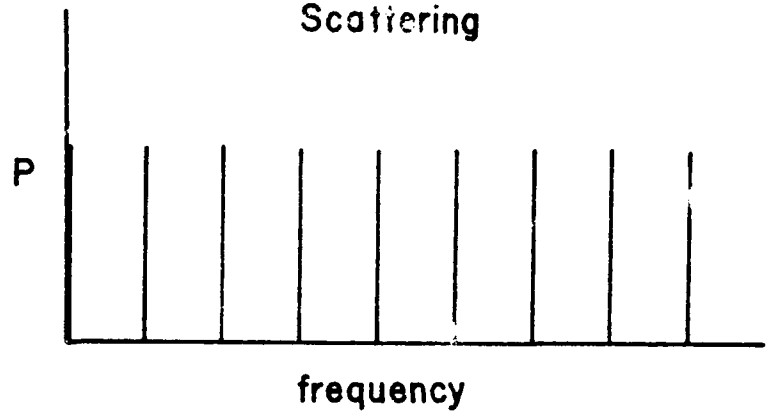
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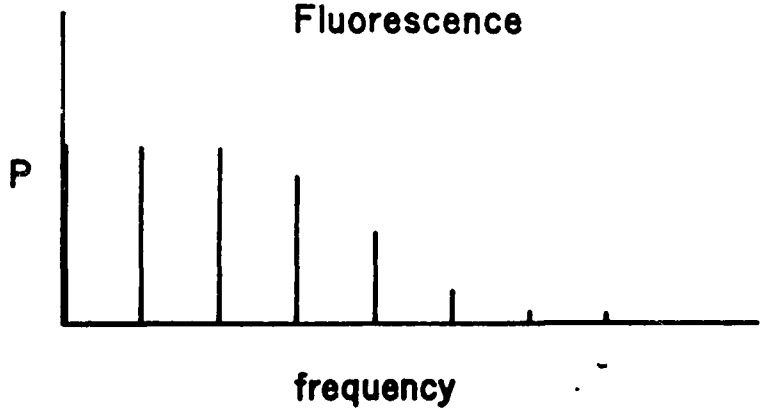
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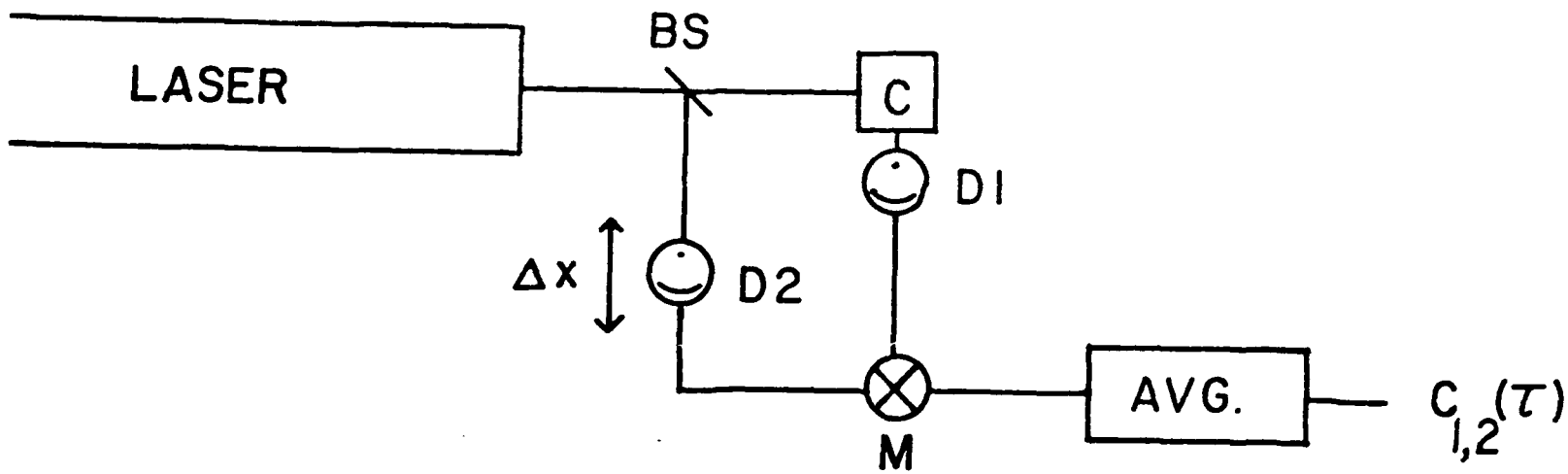
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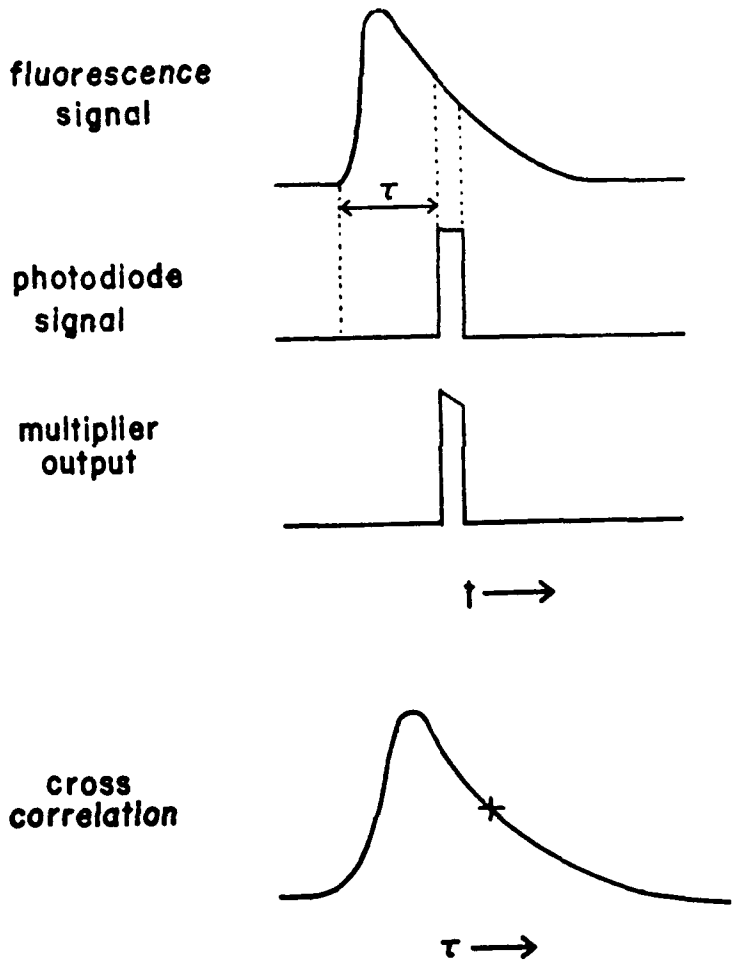
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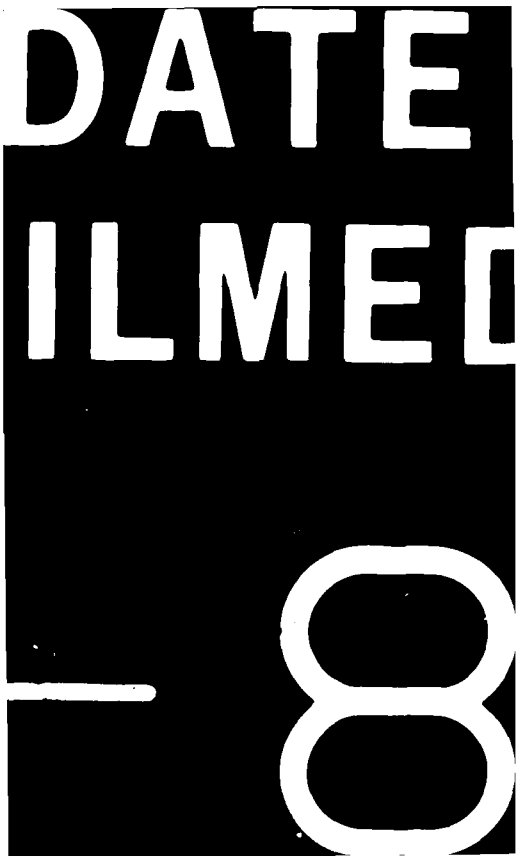
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